

Pyrethroids; EPA PC Code 109701
Pyrethroid Working Group; EPA Company Code Consortium 64977
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Test Material: Multiple pyrethroids
Determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in sediment

EPA PC Code: 109701 (File)

Other PC Codes: 128825, 109702, 128831, 097805, 109303, 127901, 128897

OCSPP Guideline: 835.6200/Aquatic Field Dissipation; 850.7100/Data Reporting for Environmental Chemistry Methods

For Cambridge Environmental

Primary Reviewer: Lynne Binari

Signature:

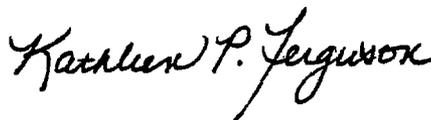


Date:

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11/09/2011

USEPA/OPP Environmental Fate and Effects Division/Environmental Risk Branch 5

Final Reviewer: José L. Meléndez
Chemist

Signature:



Date:

April 20, 2012

EPA MRID Numbers 47053001/47053002 (both same ECM)

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ANALYTICAL METHOD: EPA MRID No. 47053001. Robinson, N. 2007. Residue analytical method for the determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in sediment. Report prepared by Syngenta Crop Protection, Inc., Jealott's Hill Research Centre, Bracknell, Berkshire, United Kingdom; sponsored and submitted by Pyrethroid Working Group (Consortium No. 64977), c/o Syngenta Crop Protection, Inc., Greensboro, North Carolina; 185 pages (pp. 1-3). Final report issued February 5, 2007.

ANALYTICAL METHOD: EPA MRID No. 47053002. Reed II, R. 2006. Laboratory validation: validation of the residue analytical method: "Residue analytical method for the determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in sediment". Unpublished study performed by Morse Laboratories, Inc., Sacramento, California; sponsored and submitted by Pyrethroid Working Group (Consortium No. 64977), c/o Syngenta Crop Protection, Inc., Greensboro, North Carolina; 418 pages (pp. 1-4). Morse Protocol No.: MLI-06-02 and Project No.: ML06-1286-PWG. Experimental start date April 21, 2006, and completion date May 18, 2006 (p. 7). Final report issued November 29, 2006.

INDEPENDENT LABORATORY VALIDATION: None provided.

EXECUTIVE SUMMARY

This method is designed for the quantitative determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in sediment using an external standardization method (p. 7 of MRID 47053001). The method was developed by Syngenta Crop Protection, Inc., and validated by Morse Laboratories, Inc. (p. 12 of MRID 47053002). An independent laboratory validation (ILV) was not submitted with this method.

The Agency finds that this study is supplemental. It meets the criteria for a scientifically valid method and partially satisfies the requirement for the analysis of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin in two sediments. Deficiencies include that an independent laboratory validation of this method was not provided and the test sediments were incompletely characterized.

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Method Summary: Analytes are extracted from sediment by shaking with methanol:water (1:1, v:v) and hexane, then the hexane phase, containing the recovered analytes, is cleaned up using silica solid phase extraction (Appendix 1, p. 203 of MRID 47053002). Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin are quantified by GC/MS. The ECM utilized limits of quantitation (LOQ) and detection (LOD) of 0.1 µg/kg and 0.02 µg/kg, respectively, for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and *lambda*-cyhalothrin, and 1.0 µg/kg and 0.2 µg/kg, respectively, for permethrin (p. 30 of MRID 47053002).

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Isomerization of analytes has been found to occur with some GC instrumentation (p. 21 of MRID 47053001). In those instances, addition of 0.1% (v:v) acetic acid to all samples and standards was found to prevent isomerization; however, the reported results did not utilize this technique.

COMPLIANCE

This method was conducted in compliance with USEPA GLP Standards 40 CFR, Part 160 (p. 3 of MRID 47053002). Signed and dated statements of No Data Confidentiality, GLP and Quality Assurance were provided (pp. 2-3, 5 of MRID 47053002).

A. BACKGROUND INFORMATION

The pyrethroids share similar modes of action and are considered axonic poisons. It is now well established that severe neurological symptoms of poisoning with pyrethroids in mammals and insects are the result of modification of Na⁺ channel activity (cellular pores through which sodium ions are permitted to enter the axon to cause excitation) (Matsamura, 1985).¹ Advanced electrophysiological experiments using voltage clamp and patch clamp, together with ligand binding and ionic flux experiments, have unveiled unique actions of pyrethroids of keeping the Na⁺ channel in the open state for an extremely long period, sometimes as long as several seconds. This modification of Na⁺ channel properties leads to hyperactivity of the nervous system. Pyrethroids have also been shown to suppress GABA (*gamma*-aminobutyric acid) and glutamate receptor-channel complexes and voltage-activated Ca²⁺ channels.

Relative to physiological responses, researchers have designated two types of pyrethroids, Type I (*e.g.*, bifenthrin and permethrin) and Type II (*e.g.*, cypermethrin,

¹ Matsumura, F. 1985. Toxicology of insects. 2nd ed. Plenum New York.

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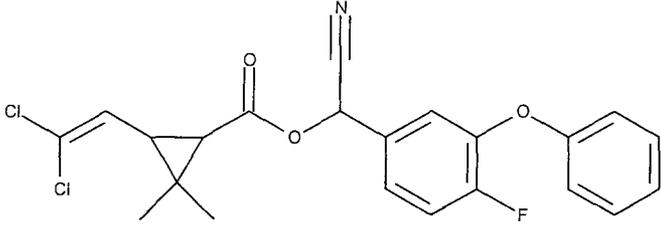
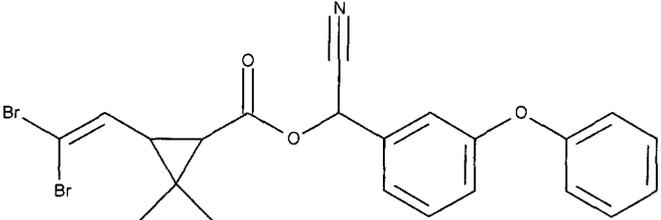
deltamethrin and fenvalerate). Structurally, Type I pyrethroids lack the *alpha*-cyano group that characterizes Type II pyrethroids. Physiologically, Type I pyrethroids typically have shorter periods of sodium channel disruption (shorter inactivation time) than that of Type II pyrethroids.

TABLE A.1. Test Compound Nomenclature	
Parameter	Value
Common name	Bifenthrin.
Company experimental name	Not reported.
IUPAC name	2-Methylbiphenyl-3-ylmethyl (Z)-(1RS,3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.
CAS Name	(2-Methyl[1,1'-biphenyl]-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	82657-04-3.
Structure	
Common name	Cypermethrin.
Company experimental name	Not reported.
IUPAC name	(RS)- α -Cyano-3-phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.
CAS Name	Cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	52315-07-8.
Structure	
Common name	Cyfluthrin.
Company experimental name	Not reported.
IUPAC name	(RS)- α -Cyano-4-fluoro-3-phenoxybenzyl (1RS,3RS;1RS,3SR)-3-

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TABLE A.1. Test Compound Nomenclature	
Parameter	Value
	(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate.
CAS Name	Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	68359-37-5.
Structure	
Common name	Deltamethrin.
Company experimental name	Not reported.
IUPAC name	(S)- α -Cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate.
CAS Name	1-[R-[1- α -(S*),3 α]]-Cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	52918-63-5.
Structure	
Common name	Esfenvalerate.
Company experimental name	Not reported.
IUPAC name	(S)- α -Cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate.
CAS Name	[S-(R*,R*)]-Cyano(3-phenoxyphenyl)methyl 4-chloro-2-(1-methylethyl)benzeneacetate.
CAS #	66230-04-4.

EPA MRID Numbers 47053001/47053002 (both same ECM)

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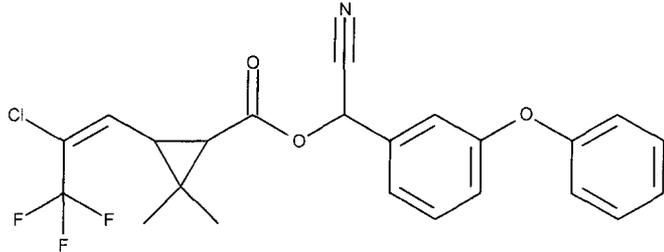
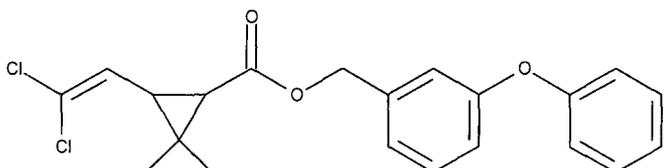
TABLE A.1. Test Compound Nomenclature	
Parameter	Value
Structure	
Common name	Fenpropathrin.
Company experimental name	Not reported.
IUPAC name	(RS)- α -Cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate.
CAS Name	Cyano(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate.
CAS #	64257-84-7.
Structure	
Common name	<i>Lambda</i>-cyhalothrin.
Company experimental name	Not reported.
IUPAC name	Reaction product of equal quantities of (S)- and (R)- α -cyano-3-phenoxybenzyl (Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.
CAS Name	[1 α (S*),3 α (Z)]-(\pm)-Cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	91465-08-6.

EPA MRID Numbers 47053001/47053002 (both same ECM)

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TABLE A.1. Test Compound Nomenclature	
Parameter	Value
Structure	
Common name	Permethrin.
Company experimental name	Not reported.
IUPAC name	3-Phenoxybenzyl (1RS,3RS;1RS,3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.
CAS Name	(3-Phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate.
CAS #	52645-53-1.
Structure	

Information obtained from pp. 15-18 of MRID 47053002.

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound	
Parameter	Value
Melting point/range (°C)	Not reported.
pH	Not reported.
Density (g/cm ³)	Not reported.
Water solubility at 20 °C (mg/L)	Not reported.
Solvent solubility at 20 °C (mg/L)	Not reported.
Vapor pressure at 25°C (torr)	Not reported.
Dissociation constant (pK _a)	Not reported.
Octanol/water partition coefficient	Not reported.
UV/visible absorption spectrum (nm)	Not reported.

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ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**B. MATERIALS AND METHODS****B.1. Principle of Method**

Analytes are extracted from sediment by mechanical shaking with methanol:water (1:1, v:v) and hexane (pp. 23-24; Appendix 1, pp. 203-205 of MRID 47053002). The hexane phase, containing the recovered analytes, is cleaned up using silica solid phase extraction (SPE). Analytes are separated and quantified by GC/MS using a Varian CP-Sil 8CB-MS column, negative ion chemical ionization (NICI) and selected ion monitoring (SIM). A confirmatory method was not utilized.

TABLE B.1. Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied

Parameter	Value
Method ID	Residue analytical method for the determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, <i>lambda</i> -cyhalothrin and permethrin in sediment (p. 23; Appendix 1, p. 194 of MRID 47053002).
Analyte(s)	Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, <i>Lambda</i> -cyhalothrin and Permethrin.
Extraction solvent/technique	Sediment (50 g) is extracted with methanol: water (1:1, v:v, 75 mL) and hexane (50 mL) via mechanical shaking for 60 minutes (pp. 22-23; Appendix 1, p. 203 of MRID 47053002). Sample is then centrifuged to disperse emulsions and separate extract phases from sediment.
Cleanup strategies	An aliquot of the hexane phase, equivalent to 10 g sediment, is taken to dryness at 40°C under an air stream (Appendix 1, pp. 203-204 of MRID 47053002). Residues are reconstituted in hexane and applied to a Varian Silica Bond Elut SPE cartridge. Analytes are eluted with hexane: diethyl ether (9:1, v:v), the eluate is taken to dryness as described above and resulting residues reconstituted in acetone containing 0.1% (v:v) peanut oil.
Instrument/Detector	Agilent 6890 GC system equipped with a Varian CP-Sil 8CB-MS column (0.25 mm x 30 m, 0.25 µm film thickness, 95% dimethylpolysiloxane:5% diphenyl) and Agilent 5973N MS system with NICI and SIM (p. 23; Appendix 1, p. 204 of MRID 47053002).

Information obtained from pp. 22-23; Appendix 1, pp. 194, 203-204 of MRID 47053002.

C. RESULTS AND DISCUSSION**C.1. Recovery Results Summary**

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TABLE C.1. Recovery Results from Method Validation for the Determination of Residues in Two Sediments			
Analyte	Spiking Level (µg/kg)	Mean Recoveries Obtained (%)	Relative Standard Deviation
California Fresh Water Sediment (TOC 1.31%)^{1,2}			
Bifenthrin	0.1	106	2.1
	1.0	107	5.8
Cypermethrin	0.1	106	2.9
	1.0	118	8.4
Cyfluthrin	0.1	106	2.6
	1.0	117	6.5
Deltamethrin	0.1	88	10
	1.0	108	6.1
Esfenvalerate	0.1	78	5.7
	1.0	112	8.4
Fenpropathrin	0.1	104	5.7
	1.0	113	3.3
<i>Lambda-cyhalothrin</i>	0.1	93	11
	1.0	112	6.6
Permethrin	1.0	100	5.2
	10.0	108	12
California Estuarine Sediment (TOC 0.86%)^{1,3}			
Bifenthrin	0.1	91	2.8
	1.0	99	5.2
Cypermethrin	0.1	103	7.8
	1.0	108	4.5
Cyfluthrin	0.1	99	8.7
	1.0	106	5.5
Deltamethrin	0.1	85	5.0
	1.0	85	13
Esfenvalerate	0.1	109	7.0
	1.0	105	6.4
Fenpropathrin	0.1	105	5.9
	1.0	105	6.0
<i>Lambda-cyhalothrin</i>	0.1	101	6.5
	1.0	104	5.4
Permethrin	1.0	106	5.4
	10.0	104	5.7
Sediments Combined⁴			
Bifenthrin	0.1	99	8.7
	1.0	103	6.8
	All data	101	7.9

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TABLE C.1. Recovery Results from Method Validation for the Determination of Residues in Two Sediments

Analyte	Spiking Level (µg/kg)	Mean Recoveries Obtained (%)	Relative Standard Deviation
Cypermethrin	0.1	104	5.8
	1.0	113	7.8
	All data	109	8.0
Cyfluthrin	0.1	102	6.8
	1.0	111	7.9
	All data	107	8.4
Deltamethrin	0.1	86	7.8
	1.0	97	15
	All data	91	14
Esfenvalerate	0.1	94	19
	1.0	108	7.9
	All data	101	15
Fenpropathrin	0.1	104	5.6
	1.0	109	5.9
	All data	107	6.1
<i>Lambda</i> -cyhalothrin	0.1	97	9.7
	1.0	108	7.2
	All data	102	9.9
Permethrin	1.0	103	5.9
	10.0	106	9.1
	All data	104	7.7

1 Sediments not further characterized (p. 29; Appendix 5, pp. 417-418 of MRID 47053002). Freshwater sediment obtained from Butte Creek, Butte County, California; estuarine sediment obtained from Paradise Cove, Marin County California (Appendix 2, pp. 387, 392 of MRID 47053002).

2 Results from Table 1, pp. 33-34 of MRID 47053002.

3 Results from Table 2, pp. 35-36 of MRID 47053002.

4 Results determined by primary reviewer using data obtained from Tables 1-2, pp. 33-36 of MRID 47053002 (DER Attachment 2).

C.1.1. Method Characteristics

TABLE C.2. Method Characteristics

Parameter	Value
Analyte(s)	Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, <i>Lambda</i> -cyhalothrin, Permethrin (p. 12 of MRID 47053002).
Limit of Quantitation (LOQ)	0.1 µg/kg for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and <i>lambda</i> -cyhalothrin (p. 30 of MRID 47053002).

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TABLE C.2. Method Characteristics	
	1.0 µg/kg for permethrin.
Limit of Detection (LOD)	0.02 µg/kg for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and <i>lambda</i> -cyhalothrin (p. 30 of MRID 47053002). 0.2 µg/kg for permethrin.
Accuracy/Precision at LOQ	Acceptance criteria (EFED-ECM 2, Version 1, December 2010, p. 5) were met at the LOQ for all analytes with matrix spike recoveries ranging between 70% to 120% and relative standard deviations of ≤20% (Tables 1-2, pp. 33-36 of MRID 47053002).
Reliability of the Method/[ILV]	An ILV of the ECM was not provided.
Linearity	Linear regression; range r = 0.9998-0.9999 (Figure 22, pp. 185-192 of MRID 47053002).
Specificity	Mean residues were detected at >30% of the LOQ in the matrix blank control samples for deltamethrin, esfenvalerate and <i>lambda</i> -cyhalothrin in the fresh water sediment, and for bifenthrin and deltamethrin in the estuarine sediment (p. 30 of MRID 47053002). For bifenthrin in the fresh water sediment, for esfenvalerate and <i>lambda</i> -cyhalothrin in the estuarine sediment, and for cypermethrin, cyfluthrin, fenpropathrin and permethrin in both sediments, any detections in the matrix blank controls were <30% of the LOQ (Tables 1-2, pp. 33-36 of MRID 47053002). Reported recoveries for fortified samples were corrected for mean residues detected in the control samples.

Information obtained from pp. 12, 30; Tables 1-2, pp. 33-36; Figure 22, pp. 185-192 of MRID 47053002.

C.2. Independent Laboratory Validation (ILV)

An ILV of the ECM was not provided.

TABLE C.3. Recovery Results of the Method Obtained by an Independent Laboratory Validation for the Determination of Residues in [Matrix]			
Analyte	Spiking Level (units)	Mean Recoveries Obtained (%)	Relative Standard Deviation
An Independent Laboratory Validation (ILV) was not conducted.			

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D. CONCLUSION

This environmental chemistry method (ECM) is designed for the quantitative determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, *lambda*-cyhalothrin and permethrin. The Agency finds that this study is supplemental. The ECM meets the criteria for a scientifically valid method and partially satisfies the data requirement for residues of eight synthetic pyrethroids in two sediments, given the following information is provided and found acceptable.

- **An independent laboratory validation (ILV) report for the ECM, performed by scientists differing from those who developed the original ECM,**
- Test sediments characterization, and
- Further information regarding how the LOD and LOQ were determined.

MRIDs 47053001 and 47053002 were submitted concurrently. Upon initial review, MRID 47053001 appeared to be the ECM, with MRID 47053002 the supporting Independent Laboratory Validation (ILV). However, comparison of data found that the two MRIDs contained the same results. MRID 47053002 is the ECM as performed by Morse Laboratories, Inc. MRID 47053001 presents all the same data generated by Morse Labs, but with all references to Morse Labs, including Morse Protocol and Laboratory Project Numbers, removed. The method presented in MRID 47053001 does include a section addressing the potential problem of analyte isomerization that was not included as part of the method description in MRID 47053002.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

**ENVIRONMENTAL CHEMISTRY METHOD (ECM)
 STANDARD EVALUATION PROCEDURE (SEP) CHECKLIST:
 BACKGROUND AND INITIAL REVIEW INFORMATION**

Referenced page numbers are from MRID 47053002, except where noted otherwise.
 Cited pages appear in the bottom most right corner of each page for both MRIDs.

I. Background Information

A.	Title of Method	Residue analytical method for the determination of residues of bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, <i>lambda</i> -cyhalothrin and permethrin in sediment (p. 12).	
B.	ECM No. [BEAD]		
C.	MRID No.	47053001 and 47053002: These documents were submitted concurrently. Upon initial review, MRID 47053001 appeared to be the ECM, with MRID 47053002 the supporting ILV. However, comparison of data found that the two MRIDs contained the same results. MRID 47053002 is the ECM as performed by Morse Laboratories, Inc. MRID 47053001 presents all the same data generated by Morse Labs, but with all references to Morse Laboratories, including Morse Protocol and Laboratory Project Numbers, removed. MRID 47053001 lists the study "Performer" as Syngenta Crop Protection, Inc., Jealott's Hill Research Centre. MRID 47053002 lists Syngenta Crop Protection, Inc., Jealott's Hill Research Centre as the study monitor (p. 6; Appendix 2, p. 377). The method presented in MRID 47053001 includes a section addressing the potential problem of analyte isomerization (see section IV. Detailed Information about the Method C. 8. a below) that was not included as part of the method description in MRID 47053002.	
D.	Matrix	Sediment.	
E.	Analyte(s) detected	Compounds:	Bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, <i>lambda</i> -cyhalothrin, permethrin

Information obtained from pp. 12, 15-18 of MRID 47053002. For structures, see the review report.

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II. Information about the Laboratory

A.	Name	Morse Laboratories, Inc. (p. 1).
B.	Address	1525 Fulton Avenue, Sacramento, California, 95825.
C.	Telephone No.	Not reported.
D.	Name of the Study Director	Richard L. Reed II (p. 7).
E.	Name of the Lead Chemist	Kevin Clark, Chief GC Chemist (p. 7).
F.	Laboratory Validation:	Yes, at LOQ and 10 x LOQ (p. 12).

Information obtained from pp. 1, 7, 12 of MRID 47053002.

III. Method Summary Information for Analyte(s): Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-cyhalothrin and Permethrin.

A.	Statement of Data Confidentiality	Yes (p. 2).
1.	Is the Method Classified or Confidential?	No.
2.	Submitted Prior to 2008 with a Non-Standard Claim of Confidentiality?	No.
B.	Sample Preparation	Rocks and plant debris removed manually (p. 21). Thoroughly mix sediment to homogenize prior to aliquot removal (p. 23; Appendix 1, p. 202). At each fortification level (LOQ, 10 x LOQ), samples were fortified with all eight analytes using a mixed standard solution (p. 22).
C.	Sample Extraction	Sediment aliquot (50 g) weighed into centrifuge bottle; add 75 mL methanol: water (1:1, v:v) and 50 mL hexane; shake on mechanical shaker for 60 minutes (p. 23; Appendix 1, p. 203). Centrifuge sample at speed to disperse emulsions and separate extract phases from sediment (e.g. 4,000 rpm, 5 minutes).

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D.	Sample Cleanup	An aliquot (10 mL) of the hexane phase, equivalent to 10 g sediment, is taken to dryness at 40°C under an air stream (Appendix 1, p. 203). Residues are reconstituted in hexane (2 mL) and applied to a solid phase extraction cartridge (Varian Silica Bond Elut, 500 mg, 3 mL). Analytes are eluted with hexane: diethyl ether (9:1, v:v, 6 mL), the eluate is taken to dryness as described above and resulting residues reconstituted in acetone containing 0.1% (v:v) peanut oil (1 mL).		
E.	Sample Derivatization	Not applicable.		
F.	Sample Analysis	GC with mass selective detection using negative ion chemical ionization (GC-MS/NICI, GC-MSD; pp. 23-25; Appendix 1, pp. 204-206).		
1.	Instrumentation	Agilent 6890 GC system with split/splitless injector and Agilent 5973N MS system using negative chemical ionization mode (p. 23; Appendix 1, p. 204).		
2.	Primary Column	Varian CP-Sil 8CB-MS column (0.25 mm x 30 m, 0.25 µm film thickness, 95% dimethylpolysiloxane: 5% diphenyl; p. 23; Appendix 1, p. 204).		
3.	Confirmatory Column	None reported.		
4.	Detector	Selected Ion Monitoring (SIM; p. 24; Appendix 1, p. 205).		
5.	Other Confirmatory Techniques	In addition to the retention time and the target ion, one qualifier ion was listed for esfenvalerate and permethrin, and two qualifier ions for bifenthrin, cyfluthrin, cypermethrin, deltamethrin and <i>lambda</i> -cyhalothrin; however, no results for the qualifier ions were reported (p. 24). Only the target ion was listed for fenpropathrin.		
6.	Other Relevant Information	Compound	Ion monitored (m/z)	Retention time(s) (minutes) ¹
		Bifenthrin	386	18.1
		Fenpropathrin	141	18.5
		<i>Lambda</i> -cyhalothrin	205	19.6 19.9
		Permethrin	207	21.5 21.8

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		Cyfluthrin	207	22.5 22.7 22.8 22.9
		Cypermethrin	207	23.2 23.4 23.5 23.6
		Esfenvalerate	211	24.9 25.3
		Deltamethrin	297	25.9 26.3
G.	Detection and Quantitation Limits			
1.	Limit of Quantitation (LOQ)			
	Claimed in Method	0.1 µg/kg for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, and <i>lambda</i> -cyhalothrin (p. 30). 1.0 µg/kg for permethrin.	Estimated	No. LOQ defined as lowest concentration of analyte yielding mean recovery of 70-110% with a relative standard deviation of ≤20% (Appendix 1, p. 210).
2.	Limit of Detection (LOD)			
	Claimed in Method	0.02 µg/kg for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, and <i>lambda</i> -cyhalothrin (p. 30). 0.2 µg/kg for permethrin.	Estimated	Yes. LOD defined as lowest concentration of analyte detectable above mean amplitude of background noise in an untreated sample at the corresponding retention time; estimated at three times background noise (Appendix 1, p. 210).

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H. Recovery (Accuracy) /Precision Data; percent recovery (mean, SD, RSD, n = 5)²									
Level ³	Cmpd ⁴	Bifen-	Cyper-	Cyflu-	Delta-	Esfen-	Fenpro-	Lambda-	Per-
California Fresh Water Sediment (TOC 1.31%)⁵									
LOQ	Range	103-109	102-110	101-108	78-102	73-84	94-108	83-108	94-108
	Mean	106	106	106	88	78	104	93	100
	SD	2.2	3.0	2.8	8.9	4.5	5.9	10	5.2
	RSD	2.1	2.9	2.6	10	5.7	5.7	11	5.2
10 x LOQ	Range	100-115	105-130	108-127	99-116	99-122	108-116	104-121	93-124
	Mean	107	118	117	108	112	113	112	108
	SD	6.3	9.9	7.6	6.5	9.4	3.7	7.4	13
	RSD	5.8	8.4	6.5	6.1	8.4	3.3	6.6	12
California Estuarine Sediment (TOC 0.86%)⁵									
LOQ	Range	87-94	96-114	89-108	78-89	97-118	95-111	90-106	98-111
	Mean	91	103	99	85	109	105	101	106
	SD	2.5	8.0	8.6	4.2	7.7	6.2	6.5	5.7
	RSD	2.8	7.8	8.7	5.0	7.0	5.9	6.5	5.4
10 x LOQ	Range	93-106	102-114	98-113	74-97	95-112	98-114	97-111	96-111
	Mean	99	108	106	85	105	105	104	104
	SD	5.1	4.8	5.8	11	6.7	6.3	5.6	5.9
	RSD	5.2	4.5	5.5	13	6.4	6.0	5.4	5.7

Information obtained from pp. 2, 21-25, 29-30; Tables 1-2, pp. 33-36; Appendix 1, pp. 202-206, 210; Appendix 5, pp. 417-418 of MRID 47053002.

1 Multiple retention times are for individual isomer peaks of the pyrethroid analyte; peak areas of each isomer were combined to determine total residue value (p. 25; Appendix 1, p. 206 of MRID 47053002).

2 Results from Tables 1-2, pp. 33-36 of MRID 47053002; verified by primary reviewer (DER Attachment 2).

3 LOQ and 10 x LOQ 0.1 and 1.0 µg/kg, respectively, for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin and *lambda*-cyhalothrin, and 1.0 and 10.0 µg/kg, respectively, for permethrin.

4 Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, *Lambda*-cyhalothrin and Permethrin, respectively.

5 Sediments not further characterized (p. 29; Appendix 5, pp. 417-418 of MRID 47053002). Freshwater sediment obtained from Butte Creek, Butte County, California; estuarine sediment obtained from Paradise Cove, Marin County, California (Appendix 2, pp. 387, 392 of MRID 47053002).

IV. Detailed Information about the Method

		YES	NO	REVIEW FURTHER
A.	Does the method require spiking with the analytes of interest?		x	pp. 21-22.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
B.	If the method requires explosive or carcinogenic reagents, are proper precautions explained?			Not applicable.
C.	Is the following information supplied?			
1.	Detailed stepwise description of:			
a.	The sample preparation procedure?	x		p. 21; Appendix 1, p. 202.
b.	The sample spiking procedure?		x	p. 22 fortification of sediments
c.	The extraction procedure?	x		p. 23; Appendix 1, p. 203.
d.	The derivatization procedure?			Not applicable.
e.	The clean-up procedure?	x		p. 23; Appendix 1, p. 203.
f.	The analysis procedure?	x		pp. 23-25.
2.	Procedures for:			
a.	Preparation of standards?	x		pp. 20-21.
b.	Calibration of instrument?	x		p. 22.
3.	List of glassware and chemicals	x		Appendix 1, pp. 212-213.
a.	Are sources recommended?	x		
b.	Are they commercially available?	x		
4.	Name, model, etc., of the instrument, column, detector, etc., used?	x		
a.	Are sources recommended?	x		
b.	Are they commercially available?	x		
5.	LOD			
a.	Is there an explanation of how it was calculated?	x		Appendix 1, p. 210.
b.	Is it a scientifically accepted procedure?			Not determined statistically (p. 30).

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
c.	Is the matrix blank free of interference at the retention time, wavelength, etc., of the analytes of interest?	<u>Freshwater sediment:</u> bifenthrin, cypermethrin, cyfluthrin, fenpropathrin, permethrin (Table 1, pp. 33-34). <u>Estuarine sediment:</u> fenpropathrin, permethrin (Table 2, pp. 35-36).	<u>Freshwater sediment:</u> deltamethrin, esfenvalerate and <i>lambda</i> -cyhalothrin. <u>Estuarine sediment:</u> bifenthrin, cyfluthrin, deltamethrin, esfenvalerate and <i>lambda</i> -cyhalothrin.	In five instances mean residues were detected at >30% of the LOQ; 0.0453, 0.0655 and 0.0414 µg/kg for deltamethrin, esfenvalerate and <i>lambda</i> -cyhalothrin, respectively, in FWS, and 0.0469 and 0.0720 µg/kg for bifenthrin and deltamethrin, respectively, in ES (p. 30). Reported recoveries for fortified samples were corrected for mean residues detected in control samples.
6.	LOQ			
a.	Is there an explanation of how it was calculated?	x		Appendix 1, p. 210.
b.	Is it a scientifically accepted procedure?			Not determined statistically (p. 30).
7.	Precision and accuracy data			
a.	Were there an adequate number of spiked samples analyzed?	x		Five replicates each at LOQ and 10 x LOQ (p. 22).
b.	Are the mean recoveries between 70-120%?	x		Tables 1-2, pp. 33-36.
c.	Are the RSDs of the replicates 20% or less at or above the LOQ?	x		

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
8.	Description and/or explanation of:			
a.	Areas where problems may be encountered?	x		Addition of 0.1% (v:v) acetic acid to all samples and standards may be required to prevent isomerization (p. 21 of MRID 47053001).
b.	Critical steps?	x		
c.	Interferences that may be encountered?	x		Disposable labware is used to prevent any cross contamination (Appendix 1, p. 209).
9.	Characterization of the Matrices?		Incomplete	Only total organic carbon reported (pp. 19, 29).

Information obtained from pp. 19-25, 29-30; Tables 1-2, pp. 33-36; Appendix 1, pp. 202-203, 209-210, 212-213 of MRID 47053002; and p. 21 of MRID 47053001.

V. Representative Chromatograms

		YES	NO	REVIEW FURTHER
A.	Are there representative chromatograms for:			
1.	Analytes in each matrix at the LOQ and 10 x LOQ?	x		Figure 4, pp. 59-65; Figure 7, pp. 80-86; Figure 12, pp. 115-121; Figure 15, pp. 136-142.
2.	Method blanks?		x	Reagent blanks were analyzed with no residues detected at the retention times of the pyrethroid analytes (Tables 1-2, pp. 33-36).

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
3.	Matrix blanks?	x		Figure 2, pp. 45-51; Figure 10, pp. 101-107.
4.	Standard curves?	x		Figure 22 (pp. 185-192).
a.	Do the standard curves have acceptable linearity?	x		r = 0.9998-0.9999).
5.	Standards that can be used to recalculate some of the values for analytes in the sample chromatograms?	x		DER Attachment 2.
B.	Can the responses of the analytes(s) in the chromatograms of the lowest spiking level be accurately measured?	x		

Information obtained from Tables 1-2, pp. 33-36; Figure 2, pp. 45-51; Figure 4, pp. 59-65; Figure 8, pp. 80-86; Figure 10, pp. 101-107; Figure 12, pp. 115-121; Figure 15, pp. 136-142; Figure 22, pp. 185-192 of MRID 47053002.

VI. Good Laboratory Practice (GLP) Standards

		YES	NO	REVIEW FURTHER
A.	Is there a statement of adherence to the FIFRA GLP standards?	x		p. 3.

Information obtained p. 3 of MRID 47053002.

VII. Independent Lab Validation (ILV)

		YES	NO	REVIEW FURTHER
A.	Was an ILV performed?		x	None provided.
B.	Was the validation independent?			None provided.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
C.	Did the ILV's precision/accuracy data meet the criteria established in OPPTS Guideline 850.7100?			None provided.
D.	Were recommendations of major or minor modifications to the method made by the independent lab performing the ILV? If major modifications were suggested, what were they?			None provided.

VIII. Completeness

		YES	NO	REVIEW FURTHER
A.	Has enough information been supplied to do a proper review?		x	ILV required.
B.	Has enough information been supplied to do a laboratory evaluation, if requested? [BEAD]			
C.	Are all steps in the method scientifically sound?	x		
D.	Is a confirmatory method or technique provided?		x	
E.	Check the category below which best describes this ECM. [Is the data supplied in the method package satisfactory or deficient in any way? If there are deficiencies, are the deficiencies major or minor? Note whether deficiencies are with the method procedure, whether they are with respect to guidelines, and whether they affect the review classification.]			
1.	Satisfactory		x	
2.	Major Deficiencies	x		ILV required.

Pyrethroids; EPA PC Code 109701 (File)
 EPA MRID Numbers 47053001/47053002 (both same ECM)

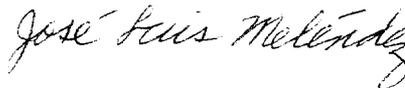
ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
3.	Minor Deficiencies	x		Confirmatory method not employed; LOD and LOQ were not determined statistically.

IX. Recommendations

- Section **VIII. Completeness E. 2. Major Deficiencies.** An independent laboratory validation (ILV) report for the ECM, performed by scientists differing from those who developed the original ECM, was not submitted with this data package and should be submitted.
- Section **VIII. Completeness E. 3. Other Deficiencies.** A confirmatory method was not provided to verify the identities of the pyrethroid analytes, the test sediments were incompletely characterized, and the LOD and LOQ were not statistically determined.

Final Reviewer: José L. Meléndez
 Chemist

Signature: 

USEPA/OPP/EFED/ERB5

Date: April 20, 2012

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Bifenthrin in two California sediments.¹

Fortified ($\mu\text{g a.i./kg}$)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0	0.103 0.106 0.107 0.107 0.109	0.103 0.106 0.107 0.107 0.109	103 106 107 107 109	106	2.2	2.1	0.0469	0.138 0.141 0.137 0.138 0.134	0.091 0.094 0.090 0.091 0.087	91 94 90 91 87	91	2.5	2.8
1.0		0.997 1.11 1.09 1.02 1.15	0.997 1.11 1.09 1.02 1.15	100 111 109 102 115	107	6.4	5.9		0.979 1.03 1.11 1.06 1.00	0.932 0.983 1.06 1.01 0.953	93 98 106 101 95	99	5.2	5.2
Overall mean				107							95			
SD				4.5							5.8			
RSD				4.2							6.1			
Max				115							106			
Min				100							87			
n =				10							10			
Soils combined:		0.1 $\mu\text{g a.i./kg}$ fortifications combined:					1.0 $\mu\text{g a.i./kg}$ fortifications combined:							
Overall mean	101						Overall mean						Overall mean	103
SD	8.0						SD						SD	7.0
RSD	7.9						RSD						RSD	6.8
Max	115						Max						Max	115
Min	87						Min						Min	93
n =	20						n =						n =	10

Results from Table 1, p. 33; Table 2, p. 35 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.



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Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Cypermethrin in two California sediments.¹

Fortified ($\mu\text{g a.i./kg}$)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0	0.107	0.107	107				0	0.0979	0.098	98			
		0.102	0.102	102					0.114	0.114	114			
		0.105	0.105	105					0.108	0.108	108			
		0.104	0.104	104					0.0955	0.096	96			
		0.110	0.110	110	106	3.0	2.9		0.0970	0.097	97	102	8.1	7.9
1.0		1.11	1.11	111					1.02	1.02	102			
		1.30	1.30	130					1.10	1.10	110			
		1.20	1.20	120					1.14	1.14	114			
		1.05	1.05	105					1.11	1.11	111			
		1.23	1.23	123	118	9.9	8.4		1.05	1.05	105	108	4.8	4.5
Overall mean				112							105			
SD				9.4							7.0			
RSD				8.4							6.7			
Max				130							114			
Min				102							96			
n =				10							10			
Soils combined:		0.1 $\mu\text{g a.i./kg}$ fortifications combined:					1.0 $\mu\text{g a.i./kg}$ fortifications combined:							
Overall mean	109	Overall mean			104	Overall mean					113			
SD	8.7	SD			6.0	SD					8.8			
RSD	8.0	RSD			5.8	RSD					7.8			
Max	130	Max			114	Max					130			
Min	96	Min			96	Min					102			
n =	20	n =			10	n =					10			

Results from Table 1, p. 33; Table 2, p. 35 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Cyfluthrin in two California sediments.¹

Fortified (µg a.i./kg)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0	0.107	0.107	107				0.0117	0.101	0.089	89			
		0.105	0.105	105					0.120	0.108	108			
		0.107	0.107	107					0.104	0.092	92			
		0.101	0.101	101					0.119	0.107	107			
		0.108	0.108	108	106	2.8	2.6		0.110	0.098	98	99	8.6	8.7
1.0		1.11	1.11	111					0.992	0.980	98			
		1.27	1.27	127					1.08	1.07	107			
		1.19	1.19	119					1.14	1.13	113			
		1.08	1.08	108					1.09	1.08	108			
		1.20	1.20	120	117	7.6	6.5		1.03	1.02	102	105	5.7	5.4
Overall mean				111							102			
SD				8.1							7.6			
RSD				7.3							7.5			
Max				127							113			
Min				101							89			
n =				10							10			
Soils combined:		0.1 µg a.i./kg fortifications combined:					1.0 µg a.i./kg fortifications combined:							
Overall mean	107	Overall mean			102	Overall mean					111			
SD	8.9	SD			6.9	SD					8.8			
RSD	8.4	RSD			6.8	RSD					7.9			
Max	127	Max			108	Max					127			
Min	89	Min			89	Min					98			
n =	20	n =			10	n =					10			

Results from Table 1, p. 33; Table 2, p. 35 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids

PC: 069007

MRID: 47053002

Guideline: 850.7100 ECM in sediment

Method validation for determination of Deltamethrin in two California sediments.¹

Fortified ($\mu\text{g a.i./kg}$)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0.0454	0.134	0.089	89				0.0720	0.159	0.087	87			
		0.123	0.078	78					0.150	0.078	78			
		0.129	0.084	84					0.161	0.089	89			
		0.131	0.086	86					0.156	0.084	84			
		0.147	0.102	102	87	8.9	10		0.158	0.086	86	85	4.2	5.0
1.0		1.09	1.04	104					0.812	0.740	74			
		1.21	1.16	116					0.879	0.807	81			
		1.16	1.11	111					1.03	0.958	96			
		1.04	0.99	99					1.04	0.968	97			
		1.14	1.09	109	108	6.5	6.0		0.844	0.772	77	85	11	13
Overall mean				98							85			
SD				13							7.7			
RSD				14							9.0			
Max				116							97			
Min				78							74			
n =				10							10			
Soils combined:		0.1 $\mu\text{g a.i./kg}$ fortifications combined:					1.0 $\mu\text{g a.i./kg}$ fortifications combined:							
Overall mean	91	Overall mean			86	Overall mean				97				
SD	12	SD			6.7	SD				15				
RSD	14	RSD			7.8	RSD				15				
Max	116	Max			102	Max				116				
Min	74	Min			78	Min				74				
n =	20	n =			10	n =				10				

Results from Table 1, p. 33; Table 2, p. 35 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Esfenvalerate in two California sediments.¹

Fortified ($\mu\text{g a.i./kg}$)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0.0656	0.141	0.075	75				0.0148	0.112	0.097	97			
		0.142	0.076	76					0.126	0.111	111			
		0.147	0.081	81					0.127	0.112	112			
		0.138	0.072	72					0.124	0.109	109			
		0.149	0.083	83	78	4.5	5.8		0.133	0.118	118	110	7.7	7.0
1.0		1.12	1.05	105					0.967	0.952	95			
		1.29	1.22	122					1.10	1.09	109			
		1.24	1.17	117					1.13	1.12	112			
		1.06	0.994	99					1.08	1.07	107			
		1.22	1.15	115	112	9.4	8.4		1.03	1.02	102	105	6.4	6.1
Overall mean			95							107				
SD			19							7.2				
RSD			20							6.7				
Max			122							118				
Min			72							95				
n =			10							10				
Soils combined:		0.1 $\mu\text{g a.i./kg}$ fortifications combined:					1.0 $\mu\text{g a.i./kg}$ fortifications combined:							
Overall mean	101			94						108				
SD	15			18					8.5					
RSD	15			19					7.9					
Max	122			118					122					
Min	72			72					95					
n =	20			10					10					

Results from Table 1, p. 34; Table 2, p. 36 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Fenpropathrin in two California sediments.¹

Fortified ($\mu\text{g a.i./kg}$)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean ($\mu\text{g/kg}$)	Measured ($\mu\text{g/kg}$)	Corrected ($\mu\text{g/kg}$)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0	0.102	0.102	102				0	0.0945	0.095	95			
		0.0938	0.094	94					0.109	0.109	109			
		0.107	0.107	107					0.106	0.106	106			
		0.108	0.108	108					0.111	0.111	111			
		0.107	0.107	107	104	5.9	5.7		0.105	0.105	105	105	6.4	6.1
1.0		1.10	1.10	110					0.984	0.984	98			
		1.15	1.15	115					1.05	1.05	105			
		1.16	1.16	116					1.14	1.14	114			
		1.08	1.08	108					1.07	1.07	107			
		1.16	1.16	116	113	3.7	3.3		0.999	0.999	100	105	6.2	5.9
Overall mean				108							105			
SD				6.8							5.9			
RSD				6.3							5.7			
Max				116							114			
Min				94							95			
n =				10							10			
Soils combined:		0.1 $\mu\text{g a.i./kg}$ fortifications combined:					1.0 $\mu\text{g a.i./kg}$ fortifications combined:							
Overall mean	107	Overall mean			104	Overall mean					109			
SD	6.5	SD			5.9	SD					6.5			
RSD	6.1	RSD			5.6	RSD					5.9			
Max	116	Max			111	Max					116			
Min	94	Min			94	Min					98			
n =	20	n =			10	n =					10			

Results from Table 1, p. 34; Table 2, p. 36 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Method validation for determination of Lambda-cyhalothrin in two California sediments.¹

Fortified (µg a.i./kg)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)						
	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD (%)	RSD (%)
0.1	0.0415	0.125	0.084	84				0.0111	0.101	0.090	90			
		0.124	0.083	83					0.117	0.106	106			
		0.137	0.096	96					0.113	0.102	102			
		0.134	0.093	93					0.115	0.104	104			
		0.149	0.108	108	92	10	11		0.116	0.105	105	101	6.5	6.5
1.0		1.10	1.06	106					0.978	0.967	97			
		1.25	1.21	121					1.06	1.05	105			
		1.17	1.13	113					1.12	1.11	111			
		1.08	1.04	104					1.07	1.06	106			
		1.22	1.18	118	112	7.4	6.6		1.00	0.989	99	103	5.7	5.5
Overall mean				102							102			
SD				13							5.9			
RSD				13							5.8			
Max				121							111			
Min				83							90			
n =				10							10			
Soils combined:		0.1 µg a.i./kg fortifications combined:					1.0 µg a.i./kg fortifications combined:							
Overall mean	102	Overall mean			97	Overall mean					108			
SD	10	SD			9.4	SD					7.8			
RSD	9.9	RSD			9.7	RSD					7.2			
Max	121	Max			108	Max					121			
Min	83	Min			83	Min					97			
n =	20	n =			10	n =					10			

Results from Table 1, p. 34; Table 2, p. 36 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids

PC: 069007

MRID: 47053002

Guideline: 850.7100 ECM in sediment

Method validation for determination of Permethrin in two California sediments.¹

Fortified (µg a.i./kg)	Fresh Water Sediment (BUCGR, TOC 1.31%)							Estuarine Sediment (Paradise Cove, TOC 0.86%)							
	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD ² (%)	RSD ³ (%)	Control Mean (µg/kg)	Measured (µg/kg)	Corrected (µg/kg)	Recovery (%)	Mean (%)	SD (%)	RSD (%)	
1.0	0	0.973	0.973	97				0	0.984	0.984	98				
		0.988	0.988	99					1.11	1.11	111				
		0.939	0.939	94					1.02	1.02	102				
		0.995	0.995	100					1.07	1.07	107				
		1.08	1.08	108	100	5.2	5.2		1.11	1.11	111	106	5.6	5.3	
10.0		9.72	9.72	97					9.58	9.58	96				
		12.4	12.4	124					10.6	10.6	106				
		10.7	10.7	107					11.1	11.1	111				
		9.32	9.32	93					10.8	10.8	108				
		11.7	11.7	117	108	13	12		10.1	10.1	101	104	6.0	5.8	
Overall mean				104							105				
SD				10							5.5				
RSD				9.9							5.3				
Max				124							111				
Min				93							96				
n =				10							10				
Soils combined:				1.0 µg a.i./kg fortifications combined:						10.0 µg a.i./kg fortifications combined:					
Overall mean	104			Overall mean		103			Overall mean		106				
SD	8.1			SD		6.1			SD		9.7				
RSD	7.7			RSD		5.9			RSD		9.1				
Max	124			Max		111			Max		124				
Min	93			Min		94			Min		93				
n =	20			n =		10			n =		10				

Results from Table 1, p. 34; Table 2, p. 36 of MRID 47053002.

Means and standard deviations calculated using Microsoft program functions =AVERAGE(A1:A2) and =STDEV(A1:A2).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 SD = Standard Deviation; determined using the "unbiased" or "n-1" method.

3 RSD = Relative Standard Deviation; calculated as (SD/mean) x 100.

Chemical: Pyrethroids

PC: 069007

MRID: 47053002

Guideline: 850.7100 ECM in sediment

Verification of reported results using GC peak area data.¹

Fortified ($\mu\text{g a.i./kg}$)	Compound	Fresh Water Sediment (BUCGR, TOC 1.31%)						Estuarine Sediment (Paradise Cove, TOC 0.86%)					
		Bracket Std 1 (peak area)	Bracket Std 2 (peak area)	Mean Std (peak area)	Measured (peak area)	Measured ($\mu\text{g/kg}$)	Reported ² ($\mu\text{g/kg}$)	Bracket Std 1 (peak area)	Bracket Std 2 (peak area)	Mean Std (peak area)	Measured (peak area)	Measured ($\mu\text{g/kg}$)	Reported ³ ($\mu\text{g/kg}$)
0.1	Bifenthrin	7454	6804	7129	7355	0.103	0.103	6312	5926	6119	8465	0.138	0.138
	Cypermethrin	7257	6027	6642	7080	0.107	0.107	6869	6254	6562	6423	0.0979	0.0979
	Cyfluthrin	10870	8872	9871	10542	0.107	0.107	10000	9051	9526	9613	0.101	0.101
	Deltamethrin	6022	5406	5714	7633	0.134	0.134	4855	4457	4656	7418	0.159	0.159
	Esfenvalerate	13421	10554	11988	16887	0.141	0.141	12026	10940	11483	12911	0.112	0.112
	Fenpropathrin	11706	9881	10794	11040	0.102	0.102	10783	10414	10599	10014	0.0945	0.0945
	Lambda-cyhalothrin	10784	9119	9952	12470	0.125	0.125	8164	7569	7867	7959	0.101	0.101
1.0	Permethrin	5857	4918	5388	5246	0.974	0.973	5435	5606	5521	5433	0.984	0.984
1.0	Bifenthrin	115423	116412	115918	57760	0.997	0.997	121315	124239	122777	60105	0.979	0.979
	Cypermethrin	90994	91267	91131	50676	1.11	1.11	111862	117395	114629	58299	1.02	1.02
	Cyfluthrin	146068	144415	145242	80574	1.11	1.11	168645	178012	173329	85979	0.992	0.992
	Deltamethrin	90699	88712	89706	48891	1.09	1.09	85238	90585	87912	35683	0.812	0.812
	Esfenvalerate	185356	181974	183665	102955	1.12	1.12	221658	234713	228186	110281	0.967	0.967
	Fenpropathrin	170037	169884	169961	93570	1.10	1.10	216355	224573	220464	108530	0.985	0.984
	Lambda-cyhalothrin	153812	154546	154179	85102	1.10	1.10	154964	162527	158746	77659	0.978	0.978
10.0	Permethrin	80094	80924	80509	39075	9.71	9.72	105832	110099	107966	51714	9.58	9.58

Results from Tables 1-2, pp. 33-36; Figures 3-8, pp. 52-93; Figures 11-16, pp. 108-149 of MRID 47053002.

Measured ($\mu\text{g/kg}$) determined using reported example calculations (pp. 25-27 of MRID 47053002).

1 Sediment source and TOC obtained from pp. 12, 19, 29 of MRID 47053002.

2 Fortified Control 11 at LOQ and Fortified Control 16 at 10 x LOQ.

3 Fortified Control 21 at LOQ and Fortified Control 26 at 10 x LOQ.

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

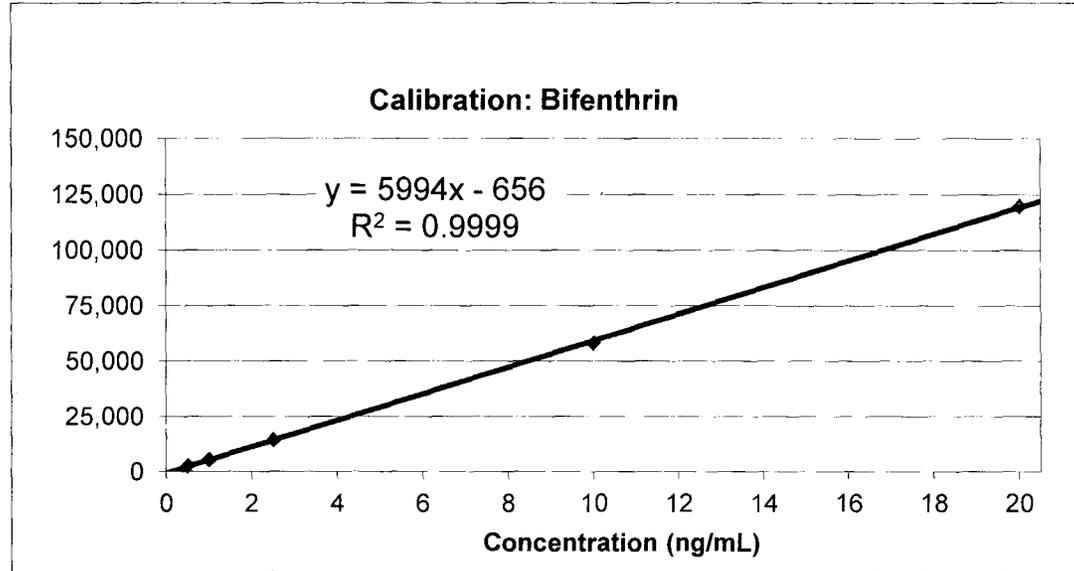
Linear regression Bifenthrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	2681
1.0	5493
2.5	14349
10	58285
20	119698

Results from Figure 17, p. 150;
 Figure 18, p. 157; Figure 19, p. 164;
 Figure 20, p. 171; Figure 21, p. 178.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999931367
R Square	0.999862738
Adjusted R Square	0.999816984
Standard Error	673.9598784
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	9926113167	9.93E+09	21853.004	6.825E-07
Residual	3	1362665.753	454221.9		
Total	4	9927475833			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-656.351068	408.4854783	-1.606792	0.2064569	-1956.3342	643.632033	-1956.33417	643.6320334
X Variable 1	5993.75751	40.54558779	147.8276	6.825E-07	5864.7234	6122.79167	5864.723354	6122.791666

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

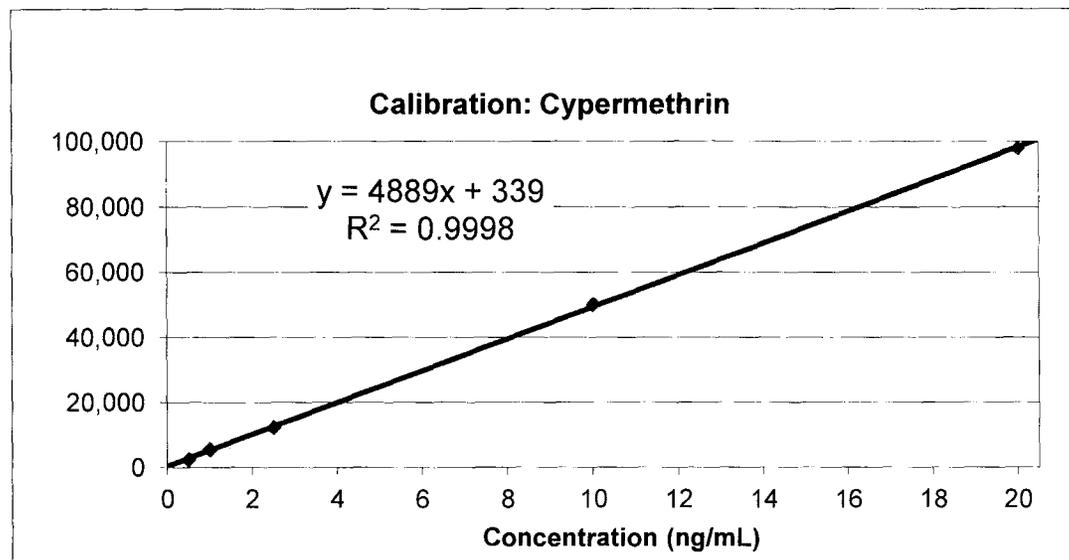
Linear regression Cypermethrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	2452
1.0	5474
2.5	12184
10	50030
20	97707

Results from Figure 17, p. 154;
 Figure 18, p. 161; Figure 19, p. 168;
 Figure 20, p. 175; Figure 21, p. 182.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999914998
R Square	0.999830003
Adjusted R Square	0.999773338
Standard Error	611.5290007
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	6598440600	6.6E+09	17644.412	9.407E-07
Residual	3	1121903.156	373967.7		
Total	4	6599562503			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	338.7278321	370.6462719	0.913884	0.4281645	-840.83403	1518.28969	-840.834026	1518.28969
X Variable 1	4886.863554	36.78973123	132.8323	9.407E-07	4769.7822	5003.9449	4769.78221	5003.944898

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

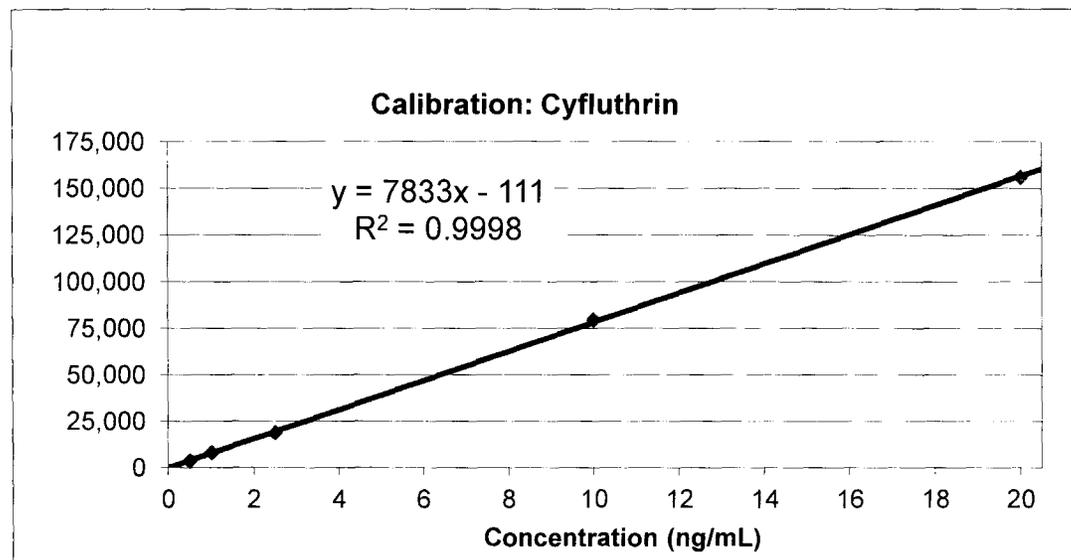
Linear regression Cyfluthrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	3564
1.0	8056
2.5	18640
10	79513
20	156003

Results from Figure 17, p. 153;
 Figure 18, p. 160; Figure 19, p. 167;
 Figure 20, p. 174; Figure 21, p. 181.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999916438
R Square	0.999832884
Adjusted R Square	0.999777179
Standard Error	971.9010229
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	16954093800	1.7E+10	17948.597	9.169E-07
Residual	3	2833774.795	944591.6		
Total	4	16956927575			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-111.4962	589.0668969	-0.189276	0.8619582	-1986.17	1763.17757	-1986.16997	1763.177569
X Variable 1	7833.337676	58.46979844	133.9724	9.169E-07	7647.2607	8019.41467	7647.260682	8019.41467

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

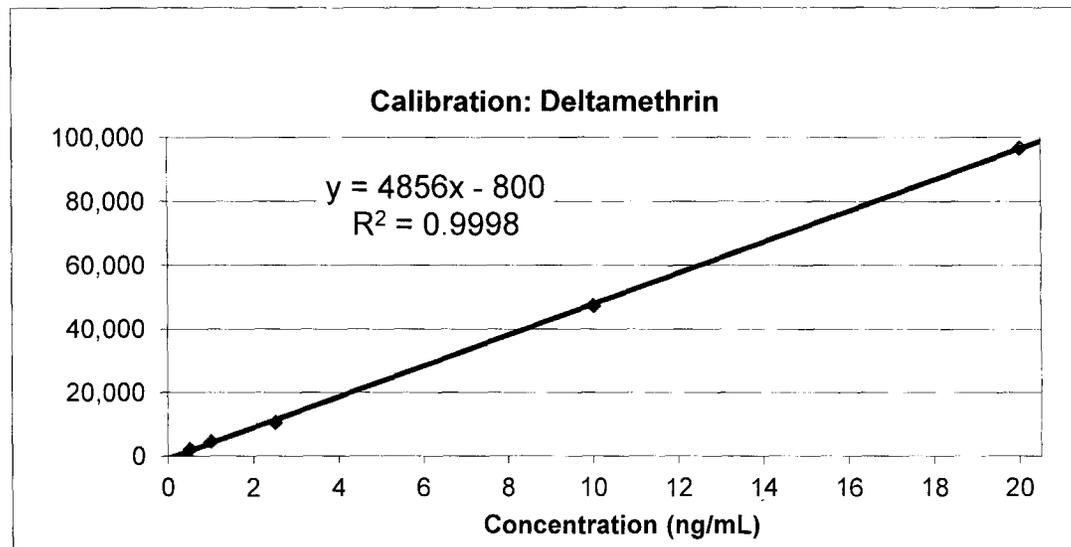
Linear regression Deltamethrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	2141
1.0	4572
2.5	10511
10	47234
20	96652

Results from Figure 17, p. 156;
 Figure 18, p. 163; Figure 19, p. 170;
 Figure 20, p. 177; Figure 21, p. 184.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.99987697
R Square	0.999753956
Adjusted R Square	0.999671941
Standard Error	731.1072057
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	6515738073	6.52E+09	12189.938	1.638E-06
Residual	3	1603553.239	534517.7		
Total	4	6517341626			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-799.764748	443.1223373	-1.80484	0.1688599	-2209.9778	610.448297	-2209.97779	610.4482966
X Variable 1	4856.141875	43.9835847	110.4081	1.638E-06	4716.1665	4996.11727	4716.166478	4996.117271

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

Linear regression Esfenvalerate.

Concentration (ng/mL)	Peak Area (counts)
0.5	4521
1.0	8960
2.5	22472
10	99991
20	197023

Results from Figure 17, p. 155;
 Figure 18, p. 162; Figure 19, p. 169;
 Figure 20 p. 176; Figure 21, p. 183.

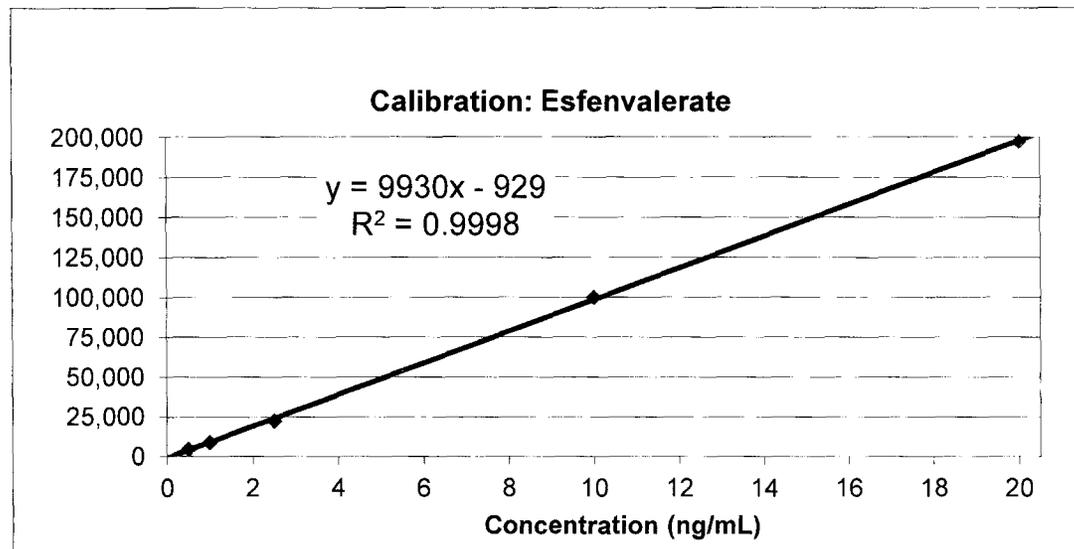
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999902578
R Square	0.999805166
Adjusted R Square	0.999740221
Standard Error	1330.282969
Observations	5

ANOVA

	df	SS	MS	F	Sig F
Regression	1	27243260859	2.72E+10	15394.693	1.154E-06
Residual	3	5308958.329	1769653		
Total	4	27248569817			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-929.022439	806.2813412	-1.152231	0.3327126	-3494.9695	1636.92464	-3494.96951	1636.924636
X Variable 1	9929.768006	80.03014218	124.0754	1.154E-06	9675.0764	10184.4596	9675.076376	10184.45964



Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

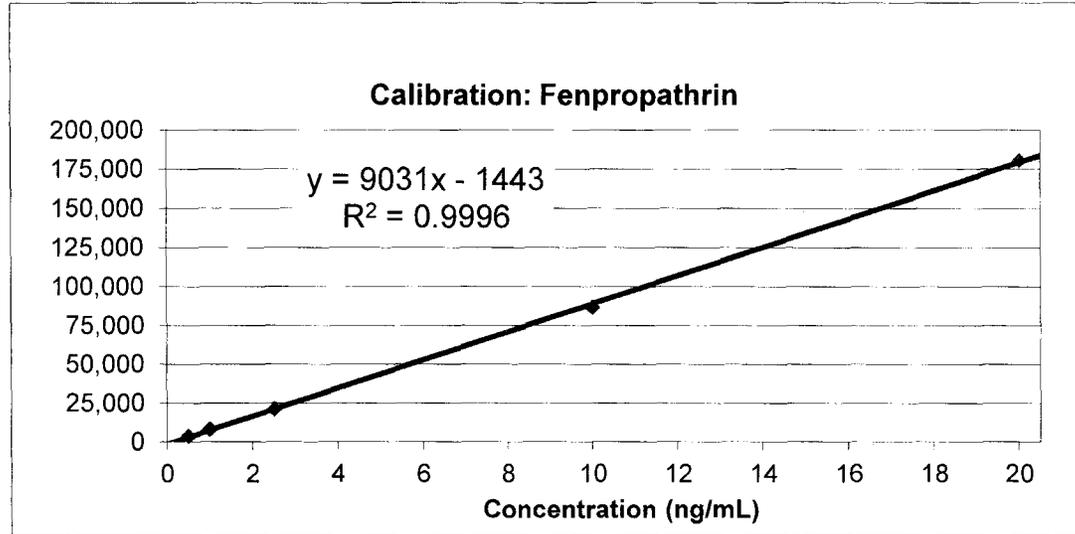
Linear regression Fenpropathrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	3802
1.0	8251
2.5	21056
10	86322
20	180408

Results from Figure 17, p. 150;
 Figure 18, p. 157; Figure 19, p. 164;
 Figure 20, p. 171; Figure 21, p. 178.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999801027
R Square	0.999602094
Adjusted R Square	0.999469459
Standard Error	1729.189356
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	22534768017	2.25E+10	7536.4702	3.369E-06
Residual	3	8970287.492	2990096		
Total	4	22543738305			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-1443.03692	1048.057554	-1.376868	0.2623099	-4778.4238	1892.34997	-4778.42381	1892.349972
X Variable 1	9031.005429	104.0284461	86.81285	3.369E-06	8699.9405	9362.07037	8699.940485	9362.070373

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

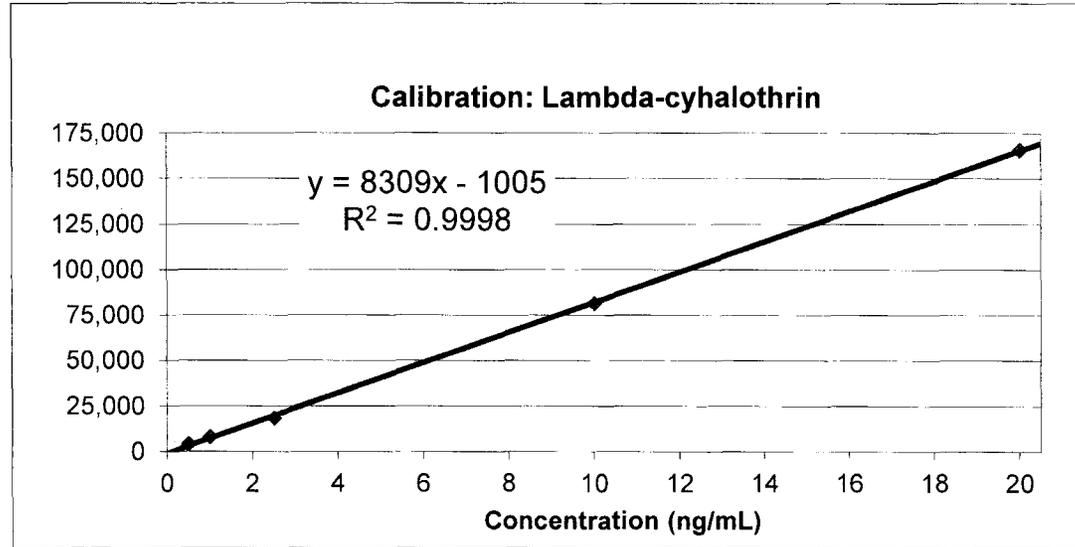
Linear regression Lambda-cyhalothrin.

Concentration (ng/mL)	Peak Area (counts)
0.5	4057
1.0	8036
2.5	18359
10	81386
20	165637

Results from Figure 17, p. 151;
 Figure 18, p. 158; Figure 19, p. 165;
 Figure 20, p. 172; Figure 21, p. 179.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.99989398
R Square	0.999787971
Adjusted R Square	0.999717295
Standard Error	1161.218192
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	19074865783	1.91E+10	14146.006	1.31E-06
Residual	3	4045283.068	1348428		
Total	4	19078911066			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-1005.09989	703.8115825	-1.428081	0.2485743	-3244.9425	1234.74268	-3244.94246	1234.742679
X Variable 1	8308.838219	69.85916471	118.937	1.31E-06	8086.5152	8531.16126	8086.515179	8531.16126

Chemical: Pyrethroids
 PC: 069007
 MRID: 47053002
 Guideline: 850.7100 ECM in sediment

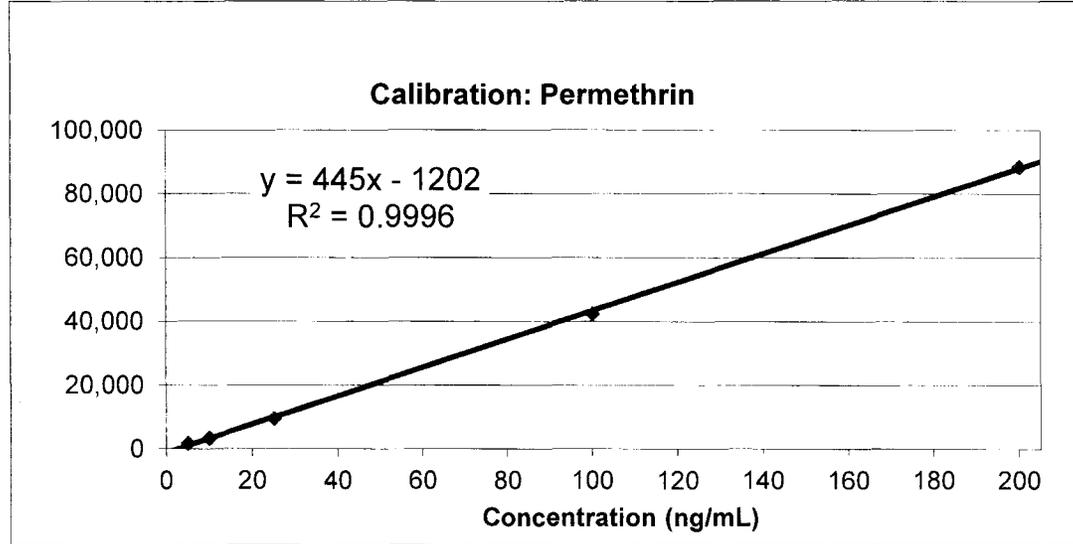
Linear regression Permethrin.

Concentration (ng/mL)	Peak Area (counts)
5.0	1788
10	3434
25	9434
100	42339
200	88355

Results from Figure 17, p. 152;
 Figure 18, p. 159; Figure 19, p. 166;
 Figure 20, p. 173; Figure 21, p. 180.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999809461
R Square	0.999618959
Adjusted R Square	0.999491945
Standard Error	834.1243105
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Sig F</i>
Regression	1	5475774812	5.48E+09	7870.1683	3.157E-06
Residual	3	2087290.096	695763.4		
Total	4	5477862102			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-1202.01013	505.5607594	-2.377578	0.0978316	-2810.9301	406.909837	-2810.9301	406.9098368
X Variable 1	445.1766196	5.018111841	88.71397	3.157E-06	429.20675	461.146491	429.2067481	461.1464911